

AD-A281 562			TION PAGE		Form Approved OMB No. 0704-0188		
1. TITLE AND SUBTITLE Title shown on Reprint			3. REPORT TYPE AND DATES COVERED Reprint		2. FUNDING NUMBERS DAAL03-92-G-0111		
4. AUTHOR(S) Author(s) listed on Reprint			7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U of North Carolina at Chapel Hill Chapel Hill, NC		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U. S. Army Research Office P. O. Box 12211 Research Triangle Park, NC 27709-2211			10. SPONSORING/MONITORING AGENCY REPORT NUMBER ARO 30377.8-GS-URT		11. SUPPLEMENTARY NOTES The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.		
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE Accession For NTIS CRA&I <input checked="" type="checkbox"/> DTIC TAB <input type="checkbox"/> Unannounced <input type="checkbox"/> Justification By Distribution/ Availability Codes Dist Avail and/or Special A-1		13. ABSTRACT (Maximum 200 words) ABSTRACT ON REPRINT 48 94-21418 259 500 DTIC QUALITY INSPECTED 8		
14. SUBJECT TERMS			15. NUMBER OF PAGES		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED		18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED		19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED		20. LIMITATION OF ABSTRACT UL	

Heterogeneous Sorption Processes in Subsurface Systems: Development and Application of Models to Batch Systems

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Introduction

Contamination of sediment, soil, and subsurface environments by hydrophobic organic compounds has led to significant research in sorption processes. Many mathematical models have been formulated for modeling the sorption process; most use a deterministic framework and assume an idealized homogeneous sorbent structure. However, natural systems display heterogeneities at scales ranging from the megascale used to describe large natural systems to the microscale of an individual grain or aggregate.

Experimental investigations of sorption processes are often conducted in batch systems in an effort to isolate the sorption process from advective and dispersive phenomena. Modeling of such systems requires a description of sorption equilibrium and rate properties. Most sorption models assume the solid phase of a bulk sample to be homogeneous with respect to sorption equilibrium and rate properties, although many experimental investigations have demonstrated otherwise.

This article provides an overview of models formulated to address sorption equilibrium and rate property heterogeneities within a bulk sample. A subset of the models is fit to an experimental data set.

Sorption Models

The sorption process is assumed to be diffusion limited. The time required for a solute-sorbent system to reach equilibrium has been observed to be related to the magnitude of the equilibrium distribution relationship (Karickhoff and Morris, 1985; Brusseau and Rao, 1989), and, to some extent, particle size (Ball and Roberts, 1991a, 1991b); both observations are consistent with a diffusion-limited process. Given the variations in equilibrium distribution relationships and particle size that are possible within a bulk sample, it is not surprising that sorption modeling approaches that incorporate equilibrium distribution relationships that are measured on a bulk sample and incorporate a first-order mass

transfer rate model have met with only limited success in batch systems (e.g., Miller and Weber, 1986; Wu and Gschwend, 1986). An instantaneous equilibrium fraction is often incorporated into rate modeling of batch systems to improve model fits (e.g., Miller and Weber, 1986; Ball and Roberts, 1991b). The need to use an instantaneous equilibrium fraction in rate modeling of batch systems is likely to be a result of model misspecification caused by variations in sorption equilibrium and rate properties at the grain scale.

The first type of models that we have formulated is an extension of diffusion-type models. The diffusion process can be modeled by Fick's law for a well-defined geometry or by a first-order mass transfer approximation.

Diffusion models based on Fick's law often assume that the sorption process is controlled by pore or surface diffusion into a well-defined particle geometry, usually a sphere. Pore diffusion is envisioned to occur in the intraparticle pore spaces of minerals and aggregates. Surface diffusion is envisioned to occur along intraparticle pore walls. The pore diffusion modeling approach has been extended to include an instantaneous equilibrium fraction in an effort to improve model fits (e.g., Ball and Roberts, 1991b).

Our general model based on Fick's law incorporates the major features that have been used by other researchers. The general model formulation allows for both pore and surface diffusion, multiple particle classes with different physical properties and sorption parameters, and an instantaneous equilibrium fraction for each particle class.

First-order mass transfer model formulations for the sorption process are frequently used for modeling batch systems (e.g., Miller and Weber, 1986; Wu and Gschwend, 1986). Wu and Gschwend (1988) attempted to account for the possible effect of particle size variations within a bulk sample by allowing for multiple particle classes, with the first-order mass transfer

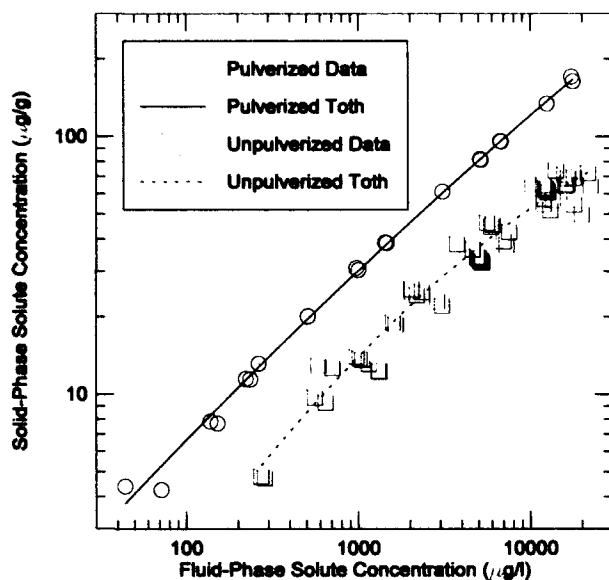


Figure 1. Experimental data and Toth model fits for the distribution of diuron at 12 weeks on pulverized and unaltered Wagner material.

coefficient for each particle class being inversely related to the square of the particle radius.

A fraction of equilibrium-type sorption sites are often included in first-order mass transfer models which have been used to model batch systems (e.g., Karickhoff and Morris, 1985; Miller and Weber, 1986). First-order mass transfer models that include a fraction of equilibrium-type sorption sites are often referred to as bicontinuum models. Physical process interpretations of bicontinuum models, often referred to as two-region or mobile-immobile fluid-phase models, assume that all of the sorption sites are at equilibrium with the adjacent fluid-phase solute concentration. However, transfer of solute between the mobile and immobile fluid phases is diffusion controlled. In our model formulation, the mobile and immobile fluid phases are viewed as the bulk and the intraparticle fluid phases, respectively. A general first-order mass transfer model, which allows for multiple particle classes with equilibrium and diffusion-controlled sorption sites, was formulated to be consistent with the general model based on Fick's law.

The two general model formulations outlined above attempt to address the variability that is possible in a bulk sample. Each particle class of a bulk sample could be assigned physical properties and sorption parameters

with these model formulations, but such an approach is impractical from an experimental and modeling perspective. A more viable approach is to describe the sorption equilibrium and rate parameters of the bulk sample with a continuous bivariate probability density function, which we have applied to a first-order mass transfer framework. In our model formulation, we assume that the sorption equilibrium and first-order mass transfer coefficients are random variables with their distribution given by the bivariate lognormal probability density function. The model can be simplified when the sorption equilibrium parameter is constant throughout the bulk sample. The simplified model describes the continuously distributed first-order mass transfer coefficient by the lognormal probability density function.

Application of Models

A subset of the models described above was fit to the results of a sorption rate experiment. Sorption equilibrium and rate experiments were conducted with the herbicide diuron on a glacially-deposited material (Wagner) with an organic carbon content of $0.22 \pm 0.02\%$. Glacially-deposited materials are typically heterogeneous with respect to particle size and origin, and the Wagner material sample is no exception.

Equilibrium experiments were conducted on unaltered and pulverized material. The material was pulverized because the use of pulverized material in

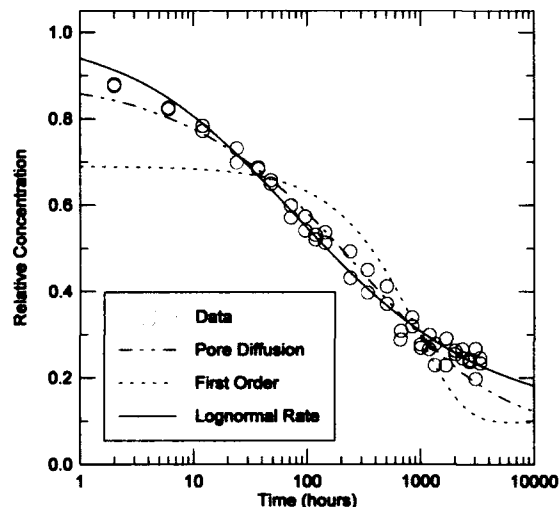


Figure 2. Experimental data and two-parameter model fits for diuron sorption on unaltered Wagner material.

sorption equilibrium experiments has been shown to substantially reduce the time required to reach equilibrium without significantly altering the final equilibrium (Ball and Roberts, 1991a, 1991b). The experiments were allowed to equilibrate for 12 weeks. The results of the equilibrium experiments on the unaltered and pulverized materials along with the Toth equilibrium model fits are shown in Figure 1. The pulverized material sorbed about 2.3 times as much as the unaltered material at a given equilibrium bulk fluid-phase solute concentration. These results suggest that the unaltered material was far from equilibrium even after 12 weeks. The equilibrium data of the pulverized material are probably more representative of true equilibrium and the Toth model fit of the results on the pulverized material was used for rate modeling.

The rate study used for the sample application of the rate models had an initial bulk fluid-phase solute concentration of $3050 \text{ mg} \times \text{L}^{-1}$, a mass of solids of 5 g, and a volume of bulk fluid of 24.9 mL. Three rate models with two adjustable parameters were fit to the data set. These models included the Fickian diffusion model with a single particle class assuming pore diffusion with an instantaneous equilibrium fraction, the first-order mass transfer model with a single particle class with an instantaneous equilibrium fraction, and the stochastic version of the first-order mass transfer model with a continuously distributed first-order mass transfer coefficient given by a lognormal probability density function. The results of the sorption rate experiment and the three model fits are shown in Figure 2. The stochastic version of the first-order mass transfer model provided the best fit to the experimental data. The pore diffusion model fit was only slightly worse, but still accurately captured the dynamics of the system. The single particle class, first-order mass transfer model with an instantaneous equilibrium fraction provided a poor fit to the data. This model overpredicts early uptake and also approaches equilibrium too rapidly.

Obviously, insight into the proper modeling approach requires additional experimental information on variations in sorption equilibrium and rate properties within a bulk sample. The time and effort involved in such detailed experimental work would be prohibitive for most investigations of sorption behavior. Barring such detailed investigations, modeling sorption rates of bulk solids in batch systems using approaches similar to the single particle class, pore diffusion model with an

instantaneous equilibrium fraction or approaches similar to the lognormally distributed first-order mass transfer model are expected to provide good descriptions of experimental results. ♦

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This work was supported by Grant DAALA03-92-G-0111 from the Army Research Office.